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Physics Procedia 22 (2011) 354 – 359

Physics Procedia

2011 International Conference on Physics Science and Technology (ICPST 2011)

Influence of Deposition Time on ZnS Thin Films Performance with Chemical Bath Deposition

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Abstract

ZnS thin films had been deposited by chemical bath deposition method onto glass substrates in alkaline liquor. The reaction solution is made of $ZnSO_4$, NH_4OH and $SC(NH_2)_2$. Different deposition times (1 h, 1.5 h, 2 h, 2.5 h and 3 h) were selected to study the performance of ZnS thin films. As the results, the ZnS films' thickness were about 50-207 nm. XRD results showed an amorphous structure. Through comparing the surface morphology before and after annealing, it could be seen that annealing made some particles grow up and the surface smooth and even. The transmittance decreased with the increase of deposition time in the range of 300-800 nm. The transmittance of annealed ZnS film was lower than that of deposited one in the range of 300-800 nm. The ZnS band gap values were calculated in the range of 3.72-3.9 eV.

Keywords: Chemical bath deposition; ZnS; Thin films; Deposition time; Annealed

1. Introduction

Recently, CdS is one of the most extensively used materials as buffer layer in solar cells based on CIGS. But CdS is a toxic material and it pollute environment in the process of production. So developing Cd-free buffer layer proves to be a focus research. ZnS thin films with a large band gap and II-VI semiconductors are promising candidates for Cd-free buffer layer. ZnS thin films were deposited by chemical bath deposition (CBD) [1-4]. The CBD method is hugely attractive because the technique possesses a number of advantages over conventional thin-film deposition methods. The main advantages of the CBD method are low cast, low deposition temperature and easy coating of large surfaces [5-7]. The band gap characteristics of the ZnS thin films are well documented: in the cubic form (lattice constant, a=0.541nm) it posse9 nm) t sses a direct band gap of 3.68 eV at 295 K and in the hexagonal form (lattice constants, a=0.382 nm and c=2.4he direct band gap is in the range of 3.74-3.87 eV at 300 K. The optical properties such as the refractive index (n) and extinction coefficient (k) of ZnS have been studied over a wide spectral range [8].

In this study, $ZnSO_4$, thiourea and ammonia solution were used as reaction solution to deposit ZnS thin films. In order to obtain good quality ZnS thin films, reaction parameters such as deposition time, temperature and concentration of $ZnSO_4$, thiourea, ammonia solution were consider. As a result, we obtained transparent and amorphous ZnS thin films with different thicknesses. Different deposition times (1 h, 1.5 h, 2 h, 2.5 h, 3 h) were selected to study the photoelectric characteristics of ZnS thin films.

2. Experimental details

2.1. Reaction mechanism

ZnS thin films had been deposited by CBD method onto glass substrates in alkaline liquor. $ZnSO_4$ and thiourea ($SC(NH_2)_2$) were used as reaction materials and ammonia solution (NH_4OH) was used as the complexing agent. Ammonia solution was controlling the Zn^{2+} concentration, following the reaction [9]:

$$Zn^{2+}+4NH_3 \leftrightarrow Zn(NH_3)_4^{2+} \quad (1)$$

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1875-3892 © 2011 Published by Elsevier B.V. Selection and/or peer-review under responsibility of Garry Lee.
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$ZnSO_4$ was used as the Zn^{2+} source and thiourea had been used as the S^{2-} source through hydrolysis in alkaline liquor [10]:

$$SC(NH_2)_2^{2+}+OH^- \leftrightarrow SH^-+CH_2N_2+H_2O \quad (2)$$

$$SH^-+OH^- \leftrightarrow S^{2-}+H_2O \quad (3)$$

During the deposition process, the ZnS films can form through two reactions:

1) $Zn(NH_3)_4^{2+}+S^{2-}+[surface\ activity\ point] \leftrightarrow ZnS+4NH_3$ (4)

Surface activity point plays a part of nuclear center. In the early stage, it was important in the growth of thin films.

2）When the unbound Zn^{2+} and S^{2-} exceeded the solubility product of ZnS, the precipitation of ZnS can occur either in solution or on the surface of the substrates:

$$Zn^{2+}+S^{2-} \leftrightarrow ZnS \quad (5)$$

In the deposition of ZnS films by the above reactions, a competitive process presented in the bath, the formation of $Zn(OH)_2$.

2.2. Deposition of ZnS films

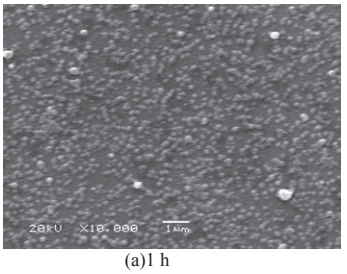
The size of glass substrates used for the deposition of ZnS films was 76 mm×26 mm×2 mm. The glass substrates were cleaned first by a mild soap solution, then washed in tap water and also washed thoroughly in deionized water. Finally, they were cleaned in alcohol. The reaction solution was made of $ZnSO_4$, NH_4OH and SC $(NH_2)_2$. The concentration of different components were $ZnSO_4$ 0.025 M, $SC(NH_2)_2$ 0.27 M, and NH_4OH 2.9 M. Firstly, $ZnSO_4$ and $SC(NH_2)_2$ were mixed in deionized water at room temperature. Secondly, NH_4OH was poured into the mixture and joined the appropriate deionized water. Lastly, the reaction solution was put into the water-bath pot at 80 °C. Different deposition times (1 h, 1.5 h, 2 h, 2.5 h, 3 h) were selected to study the characteristics of ZnS thin films. Structure, surface morphology, thickness, transmittance and the sheet resistance of ZnS thin films were measured by X ray diffraction (XRD，Cu Kα: 0.15406 nm), scanning electron microscope (SEM, JSM-6360LV), step height measurement instrument (Dektak 6M), spectrophotometer(U-3310) and four-probe detector(SX1934), respectively.

3. Results and Discussion

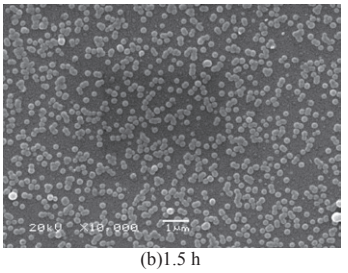
3.1. SEM results

3.1.3.SEM images of ZnS thin films with different deposition times

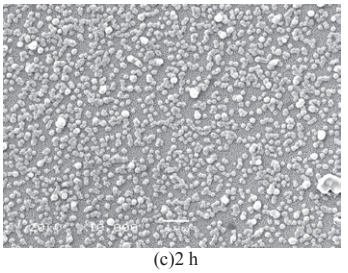
Figures 1(a)-(e) show the SEM images of annealed (200 °C) ZnS thin films with different deposition times 1 h-3 h. It could be seen in Fig.1 (a), several small particles existed on the surface. More and more large particles appeared (Fig. 1(b)-(e)) when the deposited time increased. The particles were larger than others, and the particles were sparse arrangement when the deposited time increased to 3 h (Fig.1 (e)). The average particle size increased with the increasing of deposition time. This indicates that longer deposition time will mainly bring the effect to the growth of particles with the same deposition temperature.



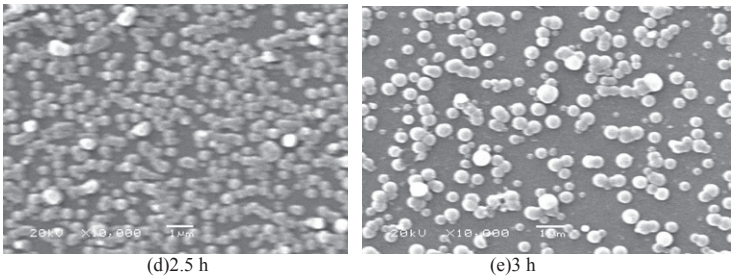
(a)1 h



(b)1.5 h



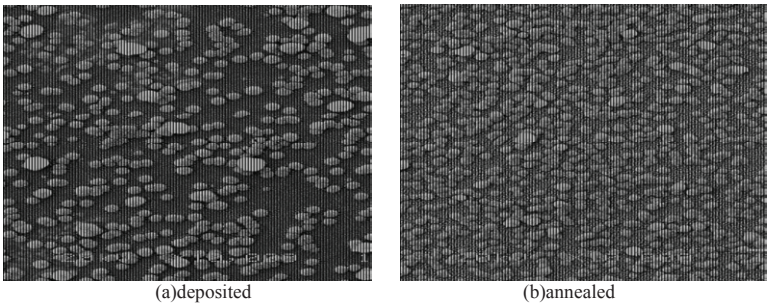
(c)2 h



(d)2.5 h (e)3 h

Fig.1. SEM images of ZnS films deposited at different times annealed at 200°C for 1 h (a)1 h, (b)1.5 h, (c)2 h,(d) 2.5 h, (e)3 h

3.1.2. The SEM images of annealed ZnS films



(a)deposited (b)annealed

Fig.2. SEM images of deposited (a) and annealed (b) ZnS films

Figure 2(a) and Fig.2 (b) is the deposited and annealed ZnS film, respectively. It could be seen that the surface morphology of the annealed ZnS film was more homogeneous, dense and the granules distribute more uniformly than the deposited one. So annealing made some particles grow up and the surface smooth and even. The larger particles could be ZnO grains as the annealing process was carried out in the air, which would lead the $Zn(OH)_2$ pyrolysis into ZnO and the small particles grew up.

3.2. Optical properties

3.2.1 .Optical transmittance spectra of different deposition times

Figure 3 shows the optical transmittance of annealed ZnS films which deposited at 80°C for 1 h-3 h. The wavelength of incident light is from 300 to 800 nm. The thickness of the films deposited at different times are 59 nm (1 h), 103 nm (1.5 h), 145 nm (2 h), 124(2.5 h), 207(3 h). It shows nearly 85% transmittance in the wavelength range of 300-800 nm at 1 h. In addition, the transmittance decreases with the increasing deposition time. This may due to the films had different thickness and roughness. It can be seen that the deposited film at short time has higher transparency, because it was thinner than the others. Moreover, this film was not densely covered by particles and the space of particles was large so the light can transmit easily. So the deposition time is very important to obtain high quality ZnS films.

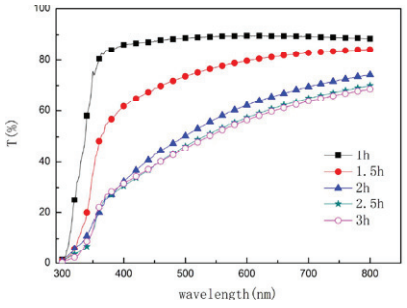


Fig.3. Optical transmittance spectra of annealed ZnS film deposited at different times

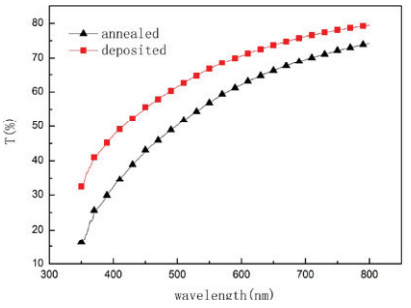


Fig.4. Optical transmittance spectra for deposited and annealed ZnS films

3.2.2. The optical transmittance spectra of annealed films

Figure 4 shows the transmittance spectra of deposited and annealed ZnS films. The deposition temperature and deposition time was 80°C and 2 h, respectively. The transmittance of annealed ZnS film was lower than that of deposited ZnS film in the range 300-800 nm. It can be seen that the annealed films had a smooth optical absorption feature. The reason was that the surface of ZnS became homogenous, and defects density decreased after annealing.

3.2.3. Optical band gap

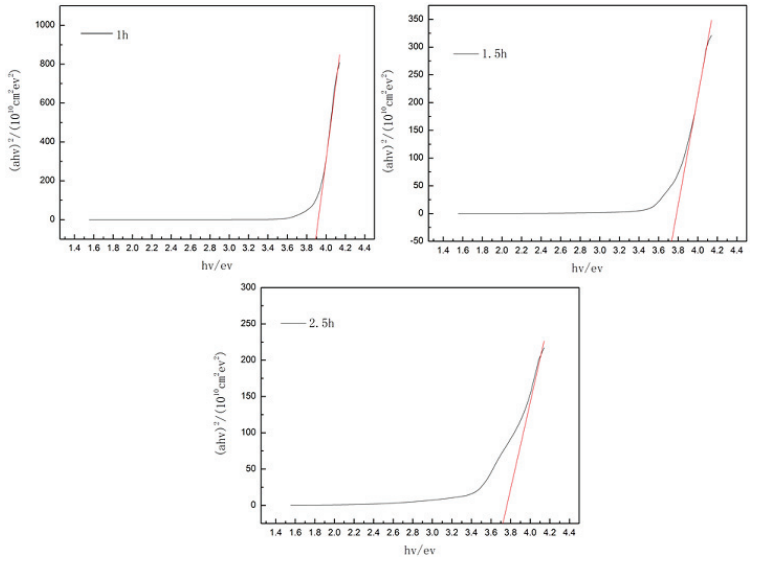


Fig.5. Curve of hv-ahv^2 of ZnS thin films deposited at different times

The optical absorption coefficient (αλ) of the films was determined from the spectral transmittance (Tλ) using the well-known relation [11]:

$$\alpha_\lambda = ln(1/T_\lambda)/d \quad (6)$$

Where d is the film thickness. ZnS is a direct allowed transition semiconductor, so its optical band gap can be estimated by Tauc formula [12]:

$$(\alpha hv)^2 = A(hv - Eg) \quad (7)$$

Where A is a constant and Eg is the corresponding semiconductor band gap. The optical band gaps of the film can evaluate from extrapolating the linear portion of the $(ahv)^2$~hv curve to the hv axis, which is illustrated in Fig.5. (a)~(c). The straight line fits show that the band gap values were in the range of 3.72-3.9 eV, which is higher than that of average value of ZnS(3.6 eV) because of quantum confinement of ZnS nanocrystals.

3.3. XRD Results

3.3.1. XRD patterns of films with different deposition times

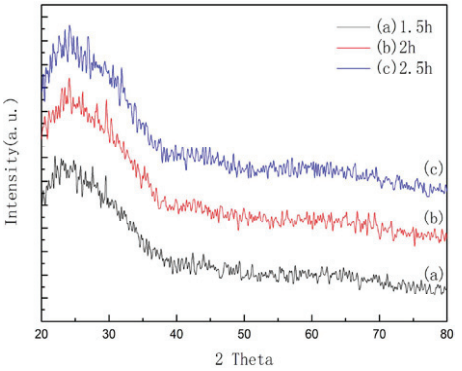


Fig.6. XRD patterns of annealed ZnS films with different deposition times (a)1.5h, (b)2h, (c)2.5h

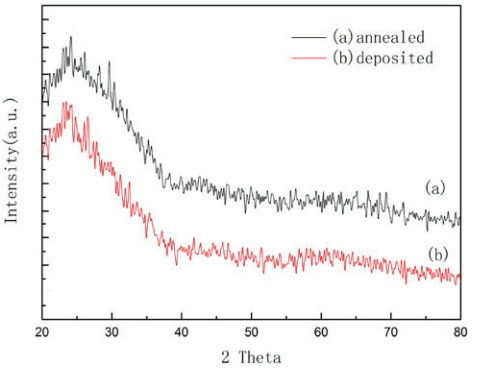


Fig.7. XRD patterns of annealed (a) and deposited (b)ZnS films

Figure 6 shows XRD patterns of the ZnS film deposited at the same deposition temperature (80 °C) and by using different deposition times for 1.5 h, 2 h and 2.5 h, respectively. (a)-(c) show a broad diffraction peak in the range of 2θ = 20-38°, which came from the glass, and no ZnS or ZnO peaks were observed. So the annealed ZnS films were still amorphous as they were very thin here and their grains were small and disordered.

3.3.2. XRD patterns of deposited and annealed ZnS films

Figure 7 shows the XRD patterns of deposited and annealed ZnS films. The XRD patterns has a broad diffraction peak, and no feature peak can be observed in the range of 2θ = 20-38°. Therefore all the deposited and annealed ZnS films were amorphous.

3.4. Film thickness and Electrical properties

Table 1 shows the thickness of the deposited and annealed ZnS films. The deposition time was 1 h-3 h. And the thickness of films is at the range of 50-207 nm. The ZnS of films' thickness with the increasing deposition time present increased. The thickness increased except 2.5 h after annealing. The reason is that the annealing process would lead the $Zn(OH)_2$ pyrolysis into ZnO and the small particles grew up in the air. The sheet resistance of ZnS films was infinite by four-probe detector. The reason is that the films were too thinner to detection.

Tab.1. Thickness of the deposited and annealed films

No.	Deposition time	Annealed thickness(nm)	Deposited thickness(nm)
1	1 h	59	50
2	1.5 h	103	78
3	2 h	145	102
4	2.5 h	124	136
5	3 h	207	189

4. Conclusions

ZnS films had been deposited by CBD with different deposition times, 1 h-3 h. The thickness of films is 50-207 nm. The films were covered with larger particles. The particles were sparsely arranged and the average particle size

increased with the increase of deposition time. This indicated that longer deposition time would mainly affect the growth of particle with the same deposition time. The XRD patterns showed that all the ZnS films were amorphous. The transmittance decreases with the increase of deposition time. Annealing reduced optical transmittance as it decreased the particles space and made particles compact. The calculated ZnS band gap values were in the range of 3.72-3.9 eV.

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